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European Patent Office

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1) Publication number:

0 649 915 A1

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wt.% Mo, 0.3 to 4 wt.% Cu, 0.05 wt.% or less N, and the		5 ,
said steel having an area ratio of a ferrite phase of a said steel having fine copper precipitates dispersed. And further a method for making the stainless steel	in a matrix. comprises austenitizing, cooling and tempering.	
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BACKGROUND OF THE INVENTION

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FIELD OF THE INVENTION

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The present invention relates to a high-strength martensitic stainless steel having excellent anti-stress corrosion cracking property and a method for making the same, and more particularly to a high-strength martensitic stainless steel showing excellent anti-stress corrosion cracking property in an environment containing CO₂ and H₂S in such a case of drilling and transporting crude oil and natural gas, and a method for making the same.

DESCRIPTION OF THE RELATED ARTS

Crude oil and natural gas recently extracted often contain large amounts of CO₂ and H₂S. To cope with this, martensitic stainless steels such as 13Cr stainless steel are adopted instead of conventional carbon steel.

Ordinary martensitic stainless steels, however, have superior corrosion resistance to CO2 (hereinafter referred to simply as "corrosion resistance") but have insufficient stress-corrosion cracking property"). Accordingly, a martensitic stainless/steel having improved anti-stress corrosion cracking property while maintaining favorable strength, toughness, and corrosion resistance has long been wanted.

Materials which satisfy the requirements of strength, toughness, and corrosion resistance, and also of anti-stress corrosion cracking property are disclosed in Examined Japanese Patent Publication No. 58-199850 and 61-207550. Those materials show a resistance to an environment containing only a slight quantity of H₂S, but they generate stress-corrosion cracking in an environment at over 0.01 atm. of H₂S partial pressure. So those materials can not be used in an environment containing a large amount of H₂S.

On the other hand, some of martensitic stainless steels which have an improved anti-stress corrosion cracking property in an environment exceeding 0.01 atm. of H₂S partial pressure are introduced a Examples of that type of martensitic stainless steel are disclosed in Unexamined Japanese Patent Publication Nosi 60-174859 and 62-54063. Those materials are however, also unable to completely prevent stress corrosion cracking caused by H₂S.

From the viewpoint of strength, a trial for improving the strength on all the martensitic stainless steels described above resulted in a significant degradation of their toughness and anti-stress corrosion cracking property.

Accordingly, all those martensitic stainless steels have an unavoidable problem in that either toughness or anti-stress corrosion cracking property is sacrificed. Asta results those martensitic stainless steels can in of be used as a deep OCTG (Oil Country Tubular Goods), for example, for which a high strength, anti-stress corrosion cracking property, anti-corrosion property, and toughness at the same time is requested.

0.06 wt.% of less C. 12 to 16 wt.% O', 1 wt % or loss S. 2 wt.% or lend 10 WANNIE THE TO YARMMUS? W. C. Mo, 0.3 to 4 wt % Ou. 0.05 wt? or leds N. and the balance being the arter materials are the second solutions.

It is an object of the present invention to provide a high-strength martensitic stainless steel which is applicable even in an environment containing a large amount of H2S while maintaining corrosion resistance by improving the conventional martensitic stainless steel in terms of strength, anti-stress corrosion cracking property, and toughness at the same time, and provides a method for making thereof. To achieve the object, the present invention provides a high strength stainless steel consisting essentially of:

0.06 wt.% or less C, 12 to 16 wt.% Cr, 1 wt.% or less Si, 2 wt.% or less Mn, 0.5 to 8 wt.% Ni, 0.1 to 2.5 wt.% Mo, 0.3 to 4 wt.% Cu, 0.05 wt.% or less N, and the balance being Fe and inevitable impurities;

said steel having an area ratio of &-ferrite phase of at most 10 %; and

said steel having fine copper precipitates dispersed in a matrix.

And the present invention provides another high strength stainless steel consisting essentially of:

0.06 wt.% or less C, 12 to 16 wt.% Cr, 1 wt.% or less Si, 2 wt.% or less Mn, 0.5 to 8 wt.% Ni, 0.1 to 2.5 wt.% Mo, 0.3 to 4 wt.% Cu, 0.05 wt.% or less N, at least one element selected from the group consisting of 0.01 to 0.1 wt.% V and 0.01 to 0.1 wt.% Nb and the balance being Fe and inevitable impurities;

said steel having an area ratio of δ-ferrite phase of 10 % or less; and said steel having fine copper precipitates dispersed in a matrix.

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The Moreover, the present invention provides a method for making a high strength stainless steel comprising the steps of: It shears hearth out the area of the

15 And the present invention provides another method for making as high strength stainless steel comprising the steps of:

preparing a martensitic stainless steel steel consisting essentially of 0.06 wt.% or less C, 12 to 16 wt.% Cr, 1 wt.% or less Si, 2 wt.% or less Mn, 0.5 to 8 wt.% Ni, 0.1 to 2.5 wt.% Mo,

20 Tto 0.3 to 4 wt. % Cti, 10.05 wt. % Tor less N, at least one element selected from the group consisting of 0.01 20 Tto 0.1 wt. % Vand 0.01 to 0.1 wt. % Novand the balance being Fe and inevitable impurities; and the balance being Fe, and inevitable impurities;

austenitizing said martensitic stainless steel at a temperature of Aca transformation point to 980 °C to produce a austenitized martensitic steel;

cooling the austenitized martensitic stainless steel;

(2) Gr 12 to 16%

tempering the cooled stainless steel to disperse fine Cu precipitate grains in a matrix at a tempering tempering the cooled stainless steel to disperse fine Cu precipitate grains in a matrix at a tempering of the properties of

BRIEF DESCRIPTION OF THE DRAWING

(3) Sr 1.0% or less

FIGURE shows the relation of the 0.2% yield stress, the Charpy impact energy, and the temper 300 parameter per general points a si is as should be seen to the constant of the seen and the presence of Si in an amount of their 10% enhances the formation of Aferita phase 35 Consequently, the Si content is specified at 1.0% of Consequently, the Si content is specified at 1.0% of Chamber Consequently.

The present invention provides a high-strength martensitic stainless steel which is applicable even in an environment containing a large amount of H₂S while maintaining corrosion resistance by improving the 40°5 conventional martensitic stainless steel in terms of strength; anti-stress corrosion cracking property, and conventional martensitic stainless steel in terms of strength; anti-stress corrosion cracking property, and conventional contains of strength; anti-stress corrosion cracking property, and conventional contains of strength; anti-stress corrosion cracking property, and conventional contains of strength; anti-stress corrosion cracking property, and conventional contains and contains contains and contains contains contain contai

Strength: The 0.2% yield stress is 75 kg/mm² or more.

(5) W (1.5 to 8.0%

Toughness: Absorbed energy on a charpy full size

Thinspecimentation of (called the Charpy impact energy) is 10 kg-m or more: not evide the eliop at leviol.

The manufaction of the charpy impact energy is 10 kg-m or more: not evide the evidence of a level of leviol.

The manufaction of the charpy impact energy is 10 kg-m or more: not evident evidence of leviol.

Anti-stress corrosion cracking property:

Generally, an increase in the strength of a steel-idegrades the toughness and anti-stress corrosion-cracking property. However, the strength can be improved without degrading the toughness and anti-stress corrosion cracking property by introducing C in an adequate amount and by dispersing Cultasic fine precipitate particles into the matrix of stainless steel through heat treatment. Since the precipitation of fine on Cultarities requires the precipitation of the tempering conditions, both the tempering temperature and togethe tempering time need to be controlled.

The present invention provides a novel martensitic stainless steel having high toughness and high strength and excellent anti-stress corrosion cracking property, which characteristics were not achieved in conventional martensitic stainless steels, while considering a restriction of the microstructure induced by the increased C content as discussed above.

15 acts. The following are, the reasons for the limitations of the present inventions cover the costs of the present inventions.

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2030/resistance cantificate state of those characteristics.

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(2) Cr: 12 to 16%

25 generates is smaller an altern presentation of a second of lasts assemble telego and princement to structure a martensitic stainless steel, and an important element to structure a martensitic stainless steel, and an important element to structure a martensitic stainless steel, and an important element to structure a martensitic stainless steel, and an important element resistance, and that above 16% induces an increase of δ-ferrite phase which, in turn, leads to a degradation in the strength and toughness even when the other alloying elements are adjusted:

25 Accordingly, the content of Cr is specified to be within a range of from 12 to 16%.

BRIEF DESCRIPTION OF THE DRAWING

(3) Si: 1.0% or less

Silicon, which functions as a de-oxidizer, is an essential element. But Si is a strong ferrite-generating element, and the presence of Si in an amount of more than 1.0% enhances the formation of δ-ferrite phase consequently, the Si content is specified as 1.0% or lessing of the definition of the presence of Si in an amount of more than 1.0% enhances the formation of δ-ferrite phase consequently, the Si content is specified as 1.0% or lessing of the definition of the presence of Si in an amount of more than 1.0% enhances the formation of δ-ferrite phase consequently, the Si content is specified as 1.0% or lessing of the definition of the presence of Si in an amount of more than 1.0% enhances the formation of δ-ferrite phase consequently, the Si content is specified as 1.0% or lessing of the definition of the presence of Si in an amount of more than 1.0% enhances the formation of δ-ferrite phase consequently, the Si content is specified as 1.0% or lessing of the definition of the presence of Si in an amount of more than 1.0% enhances the formation of δ-ferrite phase consequently.

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Nickel is quite effective for improving corrosion resistance, and for tenhancing the formation of austenite phase. However, a Ni content below 0.5% does not have the effect. Since Ni is an expensive element, the upper limit of the Ni content is specified as 8.0%.

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So When a specimen is loaded as a 60% inching of the PPE yield stress in a mixture **2.5** of **1.0**; oM₂(6), or 0.5 of 1 stress in a mixture **3.0** outlier saturated with this pass of 1 atm, the specimen is durable for 726

Mo is a particularly effective element for improving corrosion resistance. However a Mo content of less than 0.4% does not have the effect. A Mo content above 2,5% induces an excess amount of δ-ferrite phase, and so the upper limit of the Mo content is specified as 2.5% and the effect of the less and so the upper limit of the Mo content is specified as 2.5% and the effect of the less as

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Accordingly, the content of each of them is specified to a range of from 0.01 to 0.50%. A content below 0.010% does not have the effect of improving the anti-stress corrosion cracking property, and that above 0.10% has a saturating effect and increases the amount of δ-ferrite phase which, in turn, has a negative effect on the toughness. Therefore, both V and Nb are limited to a range of from 0.01 to 0.10% each.

T rempering temperature (°C)

Accordingly, the tempering time is specified by the targedfio; *0.1a:esandretinal-&locations and (0½) control 15200 to 17800. The range of from 15500 to 17000 is more preferable.

30. It be The & ferrite phase listarphase which was not transformed to martensite during the ripench thardening of the martensitie steel and was define after iterphase. An increased amount of & ferrite phase significantly degrades are the toughness. In that type of steel, if the rarea rate of the & ferrite phase exceeds 10%; the 'degradation of the toughness is considerably enhanced. Accordingly, the upper limit of the area ratio of the & ferrite phase is specified as 10%.

As for the composition of the steel of this invention the additional component Al. W. Ti. Zi., Ta. Hi. Cass or rare earth metal (IREM) may be used. There and itional elements can outline patignary and (ILI) here improvement of the performance of the steel of this invention. The purpose and adequate content of these

When precipitated in fine grains, Cu increases the strength of steel by the precipitation hardening effect without degrading the lanti-stress corrosion cracking property which susually occurs lalong with the linere ase of the strength. The term "fine precipitate" refers to grains which are identifiable by observation under an approximate size of 0.10 micron or less it. When the Cup precipitate becomes coarse and exceeds 0.10 micron, however, the effect to improving the strength diminishes. Also makens Cup does not reprecipitate and six left a dissolved in the matrix and improvement of the strength by estimation hardening can be expected. Therefore, the Cup precipitate is specified as a fine precipitate. The dispersed amount is not specifically defined. Nevertheless, it is preferable that fine precipitation exists at an entrangence of the strength and approximate of the strength.

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some application below Act pointeresults in antinsufficient austenitizing and stails to obtain necessary as the strength of the pointeresults in antinsufficient austenitizing and stails to obtain necessary at the strength of the strength of the state of the strength of the state of the strength of the state of the s

Tempering is effective for softening the martensite structure to secure toughness and also for finely precipitating Cu into the matrix to increase the strength. However, if the tempering temperature is less than 500 °C, the softening of the martensite structure is insufficient and the fine precipitation of Cu is insufficient,

and this fails to produce a steel which has the expected level of performance. On the other hand, if the tempering temperature is above Ac1, a part of the martensite structure is austenized again and the tempering is not performed to degrade the toughness. Also if the tempering temperature is above 630 °C, not the conces precipitated fines. Guagrains a dissolve ragain, and the risteel fails to exhibit sufficient of strength. It is an Gonsequently, at the attempering itemperature is specified to be within a range obstween 500 °C and eithers the solve to the strength of an analysis of the strength of

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An excessively short tempering time results in insufficient Cu precipitation and fails to obtain a sufficient strength of the steel even if the tempering temperature is kept constant. An excessively long tempering time strinduces; the coagulation and growth of coarse grains of ponce-precipitated fines Cu grains; and the Cu grains can not contribute to the improvement of the strength coadule in 200.0 evods the increase time tempering; time necessary to creatize an appropriate increase time strength is limited to as certain range. The range, however, differs dependent on each tempering temperature applied as to extend

FIGURE shows the relation of a temper parameter which is a variable function of the tempering temperature and tempering time, a 0.2% yield stress, and a Charpy impact energy. As shown in the figure, when the value of the temper parameter is within a range of from 15200 and 17800, the 0.2% yield stress is 20 31s75 kg/mm?coscmore and the Charpy impact energy is 10 tkg-m-tor-more aboth values of, which satisfy these satarget level of this invention of the temper parameter is defined by the following equation glass we also also and a sadd elimeter of the temper parameter is defined by the following equation glass with a sadd elimeter of the same as a sadd elimeter of the same and the same as a sadd elimeter of the same and the same as a sadd elimeter of the same and the same as a sadd elimeter of the same and the same as a sadd elimeter of the same as a sadd elimeter of the same and the same as a sadd elimeter of the sam

Accordingly the content of gath of them is specified to a range of them (V(273)+(273)) (273)+(2010) and that show the chart property and that are that show correspond cracking property and the effect of themselves which, in furth has a shown as the effect and increases the both V and the chart angle (number that angle (number that angle of themselves themselves themselves themselves themselves (O) (O) (O) (O) (O) (O)

Accordingly, the tempering time is specified by the tempering parameter which value is in a range of from 15200 to 17800. The range of from 15500 to 17000 is more preferable.

goid paidNow, the method; for makings the sinvention as teels will be given to the steels of this sinvention as prepared in associate the converte more any electric formace) so task to have a composition mangerias aspecified singular this inventions. The steel is a subjected to a ingote casting approcess or continuous casting approcess to form any ingote The singular undergoes should working into a seamless pipe cortains teel which is the approcessed by the at treatment. The method of heat treatment is done as described above.

As for the composition of the steel of this invention, the additional component Al, W, Ti, Zr, Ta, Hf, Carror rare earth metal (REM) may be used. These additional elements can often contribute to the further improvement of the performance of the steel of this invention. The purpose and adequate content of these improvement of the performance of the steel of this invention. The purpose and adequate content of these improvement of the performance of the steel of this invention. The purpose and adequate content of these improvements are effective actions as a stationary and the adequate content range is from 0:01 to a subtraction of the steel of this invention of the adequate content range is from 0:01 to a subtraction of the steel of the second of this invention of the adequate content is specified as 4%. This is added in an expression of the second of the s

the anti-stress corrosion cracking property of steel. Accordingly, smaller amounts of P and S are better.

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manufacture of hot-rolled steel sheets or seamless steel pipes. In A more and to bedieve a presenting sus

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	The present invention is described in more detail in the following example. The inventors prepared test
	ingots of Example steels Nos. 1 to 13 and Comparative Example steels Nos. a to j. Those ingots were
5	subjected to hot rolling to form steel sheets having a thickness of 12 mm.
	The steel sheets were then processed by heat treatment described below to obtain the test specimens.
	Less are supported by the formal production and a state of the support of the sup
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	components and an Ac ₁ and Ac ₃ transformation temperature. These steels were austenitized at 980 °C
	followed by cooling in air and tempering at 600 °C for 9 hour. The resulting steels were analyzed to
	determine the presence of δ-ferrite phase, the mechanical properties, and the anti-stress corrosion cracking
15	property. The results are summarized in Table 3. The temper parameter of the tempering in Example 1 was
15	17460. The & ferrite phase was not detected in any specimens except for the steel Nos. 5, 8, and 14 where a slight amount of 5 ferrite phase was about a ferrite phase was about a ferrite phase was about the ferrite phase was and the ferrite phase was about the ferrite phase was abo
	a slight amount of δ -ferrite phase was observed. As for the Cu precipitation, observation by an electron microscope with a magnitude of 100 000; was read to the condition of
	microscope@with a magnitude of 100,000 was conducted immediately after the tempering to confirm that fine Cu grains having the approximate size range of from 0.001 to 0.10 micron were uniformly dispersed on
	the whole matrix area. The degree of dispersion was counted as being approximately 30 to 100 fine Cu
20	precipitate grains per 1 square micron of the matrix curfoce
	precipitate grains per 1 square micron of the matrix surface. For all the steel specimens tested, the 0.2% yield stress and the Charby impact energy at 0 • C were
	above the target level 75 kg/mm² and 10 kg-m respectively. The anti-stress corresion cracking property
	above the target level, 75 kg/mm² and 10 kg-m, respectively. The anti-stress corrosion cracking property was tested and was found to conform to TMO 1-77 of the NACE (National Association of Corrosion
	Engineers () Standard Following, the procedure of the Standard, a specimen was immersed into a mixture of
25	5% NaCl solution and 0.5% acetic acid aqueous solution saturated with H2S gas of 1 atm, and the
	spēcimen was subjected to a load of 60% to the 0.2% yield stress, (for example, steel No. 1 in Table 3 was
	subjected to a load of 76 x 0.6 = 45.6 kg/mm ²). The time to failure on SSC (Sulphide Stress Corrosion test
	was determined. The results are summarized in Table 3 "SSC houre". As can be seen in Table 3, no steel
:	among the steel Nos. 1 through 16 failed before 720 hours, had passed.
<i>30</i> ,	among the steel Nos. 1 through 16 failed before 720 hours had passed. In the evaluation of the corrosion resistance to CO2, a specimen was immersed into a 10% NaCDE
į	agueous solution in an autoclave at 2005 C, 30catm., H2S partial pressure of 0.05 atm.; for 336 hours. Then,
į.	the mass loss was determined. For all the steels' Nos. 1 to 16 the mass loss was 0.5 g/m² or less, which
1	was considerably lower than 1.0 g/mm? which was the minimum required level for conventional martensite
1	stainless steels. Consequently, the steels of this invention were confirmed to have excellent corrosion
<i>3</i> 5 (resistance: 0.053 0.053 0.06 0.002 0.002 10.78 12.2 0.003 0.003. as as a constant of the const

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Table 1

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	10	-		0.025	-	; ; ;	3	-	0.005	730	630
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30	12	-	7 - 10	0:025	₃ 2;13			- a.	0.005	730	630
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50			1000T	CAR	0.5%	in and in	Acser	No.	The second second		,

The start No. 3 in Tables 1 and 2 was produced by various additionation to conference. The results are designed in a set of the same fundamental competence is designed on the same independent.

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. 50				Steel No.	Area ratio of 8- ferrite phase (%)	Diameter of Cu precipitate grain (micron)	0.2% yield stress	CVN (kg-m)	SSC (hour)	Total judgment	Note : Symbol			

55 Example 2

The steel No. 3 in Tables 1 and 2 was processed at various austenitization temperatures. The results are shown in a part of Table 4 (the austenitization temperature is designated as the quench hardening

temperature). In all cases, the steel was austenitized followed-by cooling in air, and tempering at 600 °C for 1 hour. The temper parameter at the tempering in Example 2 was 17460. When the austenitization temperature stayed with the range specified for this invention, the performance obtained was satisfactory. However, when the austenitization temperature was as low as 700 °C, the insufficient austenitization resulted in a poor performance with characteristics lower than the target level. When the austenitization temperature was as high as 1000 °C, the level of toughness obtained was low and the anti-stress corrosion cracking property was also poor?

	45	35	⁻ 30		<i>20</i> <i>25</i>	15	10	
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Fire local condition was the valued temporal temporal in a national the authorization the authorization temporal ture at 950 °C. The returns shown in a verification Alam in this case, shed No. 3 was read and the steel was austentized introved by cooling in a land record in a let 500 °C to 1 hour.

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	S (F)	^ ^	^ ^	V	V	^	^	^	^	٨		7:
10	CVN (kg-m)	13	13	7	7	10	10	13	14	13		·
15	0.2% yield stress (kg/mm²)	73	83	98	101	107	104	83	70	64		d:
20	Size of Cu precipitate (micron)		0.001-0.1 micron		No precipitation occurred		* 0	0.001-0.1 micron		No precipitation occurred		••
2 5	·		<u> </u>		Z		•	<u>-</u>	Ţ-			7,7
	J. D.		17460		14460	15460	16460	17460	18060	18460	ctory".	
30	Tempering time (hour)		1.00	ar	•			2		\$ " *	eared. tenergy at 0°C. eter. "satisfactory". "poor".	Œ.
Table 4	Tempering temperature (°C)		600		450	200	550	600	630	350	-ferrite phase appeared. the Charpy impact energy at 0°C. the fracture time. the temper parameter. of "O" means "satisfac of "X" means "poor".	∂€
40 45	Quench hardening temperature (°C)	700	900	1000			C L	000	.J.,.		In all cases, no &-ferr CVN designates the f SSC designates the f T.P. designates the i Symbol mark of Symbol mark of	9¥
50	Test Name		Example 2 (Steel No. 3)				1	Example 3 (Steel No. 3)			(Note 1) In (Note 2) CV (Note 3) SS((Note 4) T.P (Note 5) Sy	<u></u>

Example 3

The test condition was the varied tempering temperature while maintaining the austenitization temperature at 950 °C. The result is shown in a part of Table 4. Also in this case, steel No. 3 was used, and the steel was austenitized followed by cooling in air, and tempering at 600 °C for 1 hour.

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	corrosion cracking property w	as a	lsỗ þ	ocor			O	ا نهاد :	·	.01	不		•	क ठे				
5	Furthermore, no Cu preç	ipita	tion	occ	urre	d. Q	n th	e oți	her	hanç	w, k	hen th	ie tei	nperio	ng ter	npera	ture v	was 🗧
	650 °C, higher than the Ac ₁	ooint	t,⊸fin	e-C	u pre	cipi	tate!	graiˈr	าร-พู่	ere	not	prese	nt be	cause	_they	had o	dissolv	ved
	again, so the strength was de-	crea	sed.				1	}			-{	1						
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	case, steel No. 5 was austeni	ı			3 T	•		•	•	L L			_			₹		
	450 to 680 °C. The results are			ı		1		1	4	· · · · · · · · · · · · · · · · · · ·	- 1	Jg		Z E	i	, a.i.g.	<i>5</i> 0, 11	
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	However, a steel treated at the																	
	suggests that the Cu precipit											341	o res i	uiiiig	្ជាn a ២	degra	luation	1 01
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Comparative Example

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		Tempering time (hour)	14020 No	14690	15230	16000	16460	17040	17460	18070	18460 No p	19110	.00 19730	gy at 0°C. at is facto	
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35	e 5	Tempering time (hour)	0.25 14020 No	0.10 14690	0.50 15230	16000	1.00 16460	17040	1.00 17460	18070	1.00 18460 No.p	19110	5.00 19730	no &-ferrite phase appeared. tes the Charpy impact energy at 0°C. tes the fracture time. tes the temper parameter. rk of "O" means "satisfacto rrk of "X" means "poor".	3£.
35	ble 5	Tempering time (hour)	14020 No	0.10 14690	15230	16000	16460	17040	17460	18070	18460 No p	19110	.00 19730	no &-ferrite phase appeared. tes the Charpy impact energy at 0°C. tes the fracture time. tes the temper parameter. rk of "O" means "satisfacto rrk of "X" means "poor".	3£.
35	Table 5	Tempering time (hour)	0.25 14020 No	0.10 14690	0.50 15230	16000	1.00 16460	17040	1.00 17460	18070	1.00 18460 No.p	19110	5.00 19730	no &-ferrite phase appeared. tes the Charpy impact energy at 0°C. tes the fracture time. tes the temper parameter. rk of "O" means "satisfacto rrk of "X" means "poor".	3£.
35	Table 5	ing Tempering T.P.	0.25 14020 No	0.10 14690	0.50 15230	16000	1.00 16460	17040	1.00 17460	18070	1.00 18460 No.p	19110	5.00 19730	no &-ferrite phase appeared. tes the Charpy impact energy at 0°C. tes the fracture time. tes the temper parameter. rk of "O" means "satisfacto rrk of "X" means "poor".	38. Ch
35	Table 5	Temperature time (hour) T.P.	0.25 14020 No	0.10 14690	0.50 15230	16000	1.00 16460	17040	1.00 17460	18070	1.00 18460 No.p	19110	5.00 19730	to &-ferrite phase appeared. tes the Charpy impact energy at 0°C. es the fracture time. es the temper parameter. rk of "O" means "satisfacto rk of "X" means "poor".	3£.
35	Table 5	Temperature time (hour) T.P.	0.25 14020 No	0.10 14690	0.50 15230	5.00 16000	550 1.00 16460	17040	1.00 17460	18070	1.00 18460 No.p	19110	5.00 19730	In all cases, no δ -ferrite phase appeared. CVN designates the Charpy impact energy at 0°C. SSC designates the fracture time. T.P. designates the temper parameter. Symbol mark of "O" means "satisfacto Symbol mark of "X" means "poor".	38. Ch
35	Table 5	Temperature time (hour) T.P.	0.25 14020 No	0.10 14690	0.50 15230	5.00 16000	1.00 16460	17040	1.00 17460	18070	1.00 18460 No.p	19110	5.00 19730	In all cases, no δ -ferrite phase appeared. CVN designates the Charpy impact energy at 0°C. SSC designates the fracture time. T.P. designates the temper parameter. Symbol mark of "O" means "satisfacto Symbol mark of "X" means "poor".	38. Ch
35	Table 5	ture (°C) Tempering Tempering T.P. (°C)	0.25 14020 No	0.10 14690	0.50 15230	5.00 16000	550 1.00 16460	17040	1.00 17460	18070	1.00 18460 No.p	19110	5.00 19730	In all cases, no δ -ferrite phase appeared. CVN designates the Charpy impact energy at 0°C. SSC designates the fracture time. T.P. designates the temper parameter. Symbol mark of "O" means "satisfacto Symbol mark of "X" means "poor".	38. Ch

Comparative Example

Among the Comparative Examples, those which used steels having a composition which is outside the specified range of this invention are listed in Tables 6 and 7 in terms of their composition and test results. The applied austenitization temperature and tempering treatment are the same as in Example 1. Since the

steels in Table 6 had at least one component present in an amount outside of the specified range of this invention, the test results gave lower levels of strength or toughness than the target levels of this invention. As a result, the target level of this invention for the anti-stress corrosion cracking property could not be attained. Steels (a) and (b) contained Cu at below 0.3%, and no Cu precipitate was formed, which resulted in a strength of less than 75 kg/mm². Steel (c) contained Cu at above 4.0%, and it suffered cracks during the hot-rolling stage which leads to a significant degradation of the commercial value of the product. Steel (c) also showed a poor SSC characteristic. Steel (d) had a low Ni content, and steel (g) had high content of Cr and Mo, and steel (i) had a high content of Mo, so they gave delta ferrite phase over 10% of area ratio, which significantly degraded the toughness. Steel (e) had Ni content above 9%; so that the steel was very expensive.

Therefore, steel (e) was inadequate for the object of this invention. Also steel (e) was inferior in SSC performance. Steel (f) had a low Cr content and steel (h) had a low Mo content, so those steels were inferior in corrosion resistance to CO2. Steel (j) had a high C content so that the SSC performance was poor.

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	THE CALL OF A SET OF SE	* W.S.	or Site	0.02	0.21	4.61	2.63	2.61	2.62	2.61	2.55	2.62	2.55	Chand Mc	
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20		(%	ט	14.8	14.7	14.8	14.8	14.8	10.8	18.7	14.7	15.8	14.7		\
		Chemistry (wt%	Ë	4.81	4.88	4.96	0.37	9.97	4.81	1.88	4.86	4.83	4.85		
25		Che	. \$	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.005		:
·3(D	0.008	0.009	0.007	0.007	0.007	0.008	0.011	0.012	0.008	0.00	· .	3 \$j.*
38	9 a)c		Mn	0.05	0.06	0.05	0.09	0.09	0.09	0.06	0.05	0.09	0.05		. 30
	Table		Si	0.15	0.16	0.15	0.14	0.13	0.14	0.16	0.16	0.17	0.17	·	
40			C	0.024	0.026	0.023	0.024	0.025	0.024	0.026	0.025	0.024	0.085		• • • • • • • • • • • • • • • • • • • •
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12) -1 21 0 -0 SI -		' '	_	P.	1		4			The maneralic		
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15 (1967), 1 ON 100 (1967)	′ာတ်က	₹ 800 900	700	p % e-9	<u> </u>	8,2	2	100 howrs or less	Jic × €	•	æ	ž r'
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	9,	om u	u-ô	101 क्	act ener	क्षा प्रः	CDBr	more and	ig thi	Stress of 75 kg/m		
0.5 to 8 will's N. Otos	u Tha spec	ž 750								A high strength t		5- 3-50 T
goted from the group	nent sc	ଖଞ୍ଚ	10 :31	N at le	්වීම වර ල	S W	u, 0.0) % W4 %	o.3 rc	to 2.5 wt."UMo.	-	· C
ing Fe are movinable	anc <u>a</u> be	700	600	, 6 6	e e	73		•	1 1	consisting $\frac{2}{3}$ 0.0		
Labla 35		2 (1	me mite	Ditto	oitate:				saides@el ha saidestete		3£
	æ	700	60	0	o C GC	17	#	500	×	t e		
0.053 wths	91 E10 I				Z.D.O.U	12.17	clarm	ss steel of	tainle	The machinic :	12.	
2.2 to 15.8 % 9.3t of 9.2	े लक्षा १	Ac.	Ac1	phase	itate	1m ²)	claim	कि डिजाट हर	einie.	arpyin atesifr	.8%	14.
អ នៃវៈលាកប្ ^រ ័ ២ ២ មិ 47	a conto		- 24 M (A. 15	× a .	i Suissi		any	क क्षान अ		Change day	1	• ***
	No.	<u> </u>	,	ferr	ı pre icro	stress (kg	H-6	our)	dgme	desi		
patent is from 0.05 to	}	ation red(°(vitiei	of δ-fer (%)	offi in (m		CVN₹(kg-m)	SSC(hour)	opr High	The make Cath	15.	
45	O 1	rmi atu		atio	eter o grain	yield	Ü	S.	Tota	⊕ ⊕ 144 €Ω';		96
ர் is from 0 78 to 7.21	# conte	Trans <u>f</u> c temper	jerer	Arear	claire 1		anv:	°o 'eक्षंत्र उह	elnie:	The magnetic .	.15.	
ontent is from 0.30 trot	ne Mo c	i riet	ieriw i	of of the	emisio i) 500	ins (ss steer (sinima	The madensific	77	กล

^{17.} The martensitic scainless steel of any one of claims of to 16 wherein the Mo content is from 0.30 too.

^{18.} The mertensitic stamers steel of any one of claims 17 to 17 wherein said steel has an areramial 17 to 17 wherein said steel has an areramial 17 to 18 wherein said steel has an areramial 18.

^{55 1.} A high strength martensitic stainless steel consisting essentially of:

to 2.5 wt.% Mo, 0.3 to 4/wt.% Cu) 0.05 wt.% for less N, and the balance being. Fer and inevitable impurities;

		said steel ha								•		· · · · · · · · · · · · · · · · · · ·	• •	
		said steel h		rine copper	:					à	i	}		
	2.	The martensitic	stainle	ess steel of	claim	์ 🤼 า 1, w	herein	the	C cont	ent is t	from 0	.013 to (0.053 wt.%.	
5	•		imerenjes.	• • • • • • • • • • • • • • • • • • •	 		•		nya magya ga aring allahan	[}]		<u></u>		
	3.	The martensitic	stainle ∵≍	ss steel of	claim m	າຣ 1 o	r 2, w	herė	in the (Or cont	ent is	from 12	2 to 15.8 wt.%.	
	4.	The martensitic	stainle	ess steel o	fany	one (of clai	ms į	1 to 3 v	whereir	the S	Ši contei	nt is from 0.14 to 0.4	7
		wt.%.	and decimaling a	21	***************************************		•		A years - Marriag (Phinapaleophic Ambri					
10			35	13 7 8	} }	83	i •			30		† 		_
	5.		stainle	ess; st <u>e</u> el o	any	one c	of the p	prec	eding d	claims	where	in the M	n content is from 0.0)
-		to 1.05 wt.%.	***	The second secon	<u></u>	<u> </u>	ر از عن	1						
	6.	The martensitic	stainle	ess-stèel o	; f anv	one o	of the	prec	edina:	claims	where	in the N	i content is from 0.76	3
15		to 7.21 wt.%.		100	, į	•	7	' . !	3,	اسد ا	ျာလ			÷
					<u> </u>	+ 		į					å •	
	7.		stainle	ess steel-o	any	, -:	of the I	prec	eding c	claims	where	in the M	o content is from 0.30)
		to 2.42 wt.%.		do do	<u></u>	Car	-	ţ	~	ري	يَّ حَدَ			
20	£	The martensitic	etainle	es steel o	f any		of the	nrec	edina (claims	where	in said	i steel has an area ratio	∩ .
20	O.	of δ -ferrite phase					ווע וויט	prec	eunig (O	1	Steer Has all alea fath 	ار ک
		or o torres pridos	,	0 2		OC.	;		أسه	75	60	Ψ	<u>.</u>	
	9.	The martensitic	stainle	ess-steel-o	f any	-one-	of the	pre	ceding-	claims	-where	in said	steel includes at leas	t
		30 of copper pre	cipita	tes having	0.1 m	icron	or les	s in	diamet	er per	1 squa	are micr	ọn.	
25		-			· ~:	ဘ				المار) المسر	(C)	- 5		-;
•	10.	stress of 75 kg/r	-	•	1		,	· .	-	*		1	steel has 0.2 % yield	ָל
	•	suess of 75 kg/f	mii- o		Cital	ייייני אַק	haci e	ı ıcı f	jy or re	y kg-m ∴ ⇔		, i.e. }		
	11.	A high strength	marte	nsitic stainl	ı 👄 esŝ si	teel c	onsisti	ng e	essentia	ally of:	72(•	
30	Maria april 41	•	1	f F1	•			_			•	less Mn	, 0.5 to 8 wt.% Ni, 0.	1,
		3 /		~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~	•		1					•	elected from the group	
			01 to	0.12 wt. 1/2	y and	0.01	to 0.	1 w	l.% Nb	and t	he ba	lanc <u>e</u> be	ing Fe and inevitable	3
		impurities;		0 ==	; ====================================	i Securit) 	F4 MD/	or loos	·	<u> </u>		
35		said steel h	1 -				, ,	-			•	; i	5	=
		9	1×	10.1	144	1.5			0	200	100	5	1	•
	12.	The martensitic	stainle	ss ^o steel of	claim	<u>, 11, v</u>	wherei	์ก-th	e C cor	ntent is	from	0.013 to	0.053 wt.%.	
		3 3			1				T)		C	•		
	13.	The martensitic	stainle	ess steel of	claim	າຣ 11 :	or 12	whe	rein the	Cr;co	ntent	is from 1	2.2 to 15.8 wt.%.	
40	4.8	The martensitie	ctaible	es stoel of	any	- <u> </u>	i f olaic	1		where	! in tha	Ši conte	nt is from 0.14 to 0.4	~; 7
	14.	wt.%.		35 SLEET U	ally () X	i Ciaili i Ö	9		WITCHE	ייווט יוווט	Si come		,
		₹ _₹	igu	200	13	52.0	1.5	<u> </u>	<u> </u>	; ;		22		
•	15.	The martensitic	stainle	ess steelijo	fany	one	of clai	ims.	1.1-to_3	14 whe	erein t	he Min c	ontent is from 0.05 to	ס
4 5		1.05 wt.%.	. 5	000				Carrier Las	() ()			1 3	1	÷
	4.5		<u> </u>					2.	, (1) 37	i i	510		0.70 (- 7.0	
	16.	wt.%.	Stainie	ess steel of	any o	one o	r, ciaim !	រុទ្ធ T	1 to 15	wnere	n'tne	INI CONTE	ent is from 0.78 to 7.2	1
		Wt. 76.	•	1	1		:	ت	Ž.				•	
50	17.	The martensitic	stainle	ess steel o	f any	one	of clai	ims	11 to 1	16 whe	erein t	he Mo c	ontent is from 0.30 to	Q;
		2.42 wt.%.			-									
	40	The medancidic		nan ataul au	£ 00.		alai.	1	: 4 4 4 4 T	7box	-i	امید اها	han on propertional s	
	10.	ferrite phase of		_	ally	OHE C	or Ciair	пѕ	11 10 1	/ WHER	em sa	iu sieei	has an area-ratio of 8	-
55		JOINE PHASE OF	1110°C		viis in	18823	14.20	4. C1		, 23.9, PUS.)	ty ggia	ក្រុងក្នុង ពេធក្នុងព	n. A high stierigth	,
	(19.)	The martensitic	stainle										includes at least 30 c	of
7,	rt. 139	copper, precipita	tes ha	ving 0:1 m	icron!	or: les	s in d	iame	eter per	:1 squ	are m	icron. of	A Priving of the Control	
						•		•			·		. asminuami	
									• •	• •				

20. The martensitic stainless steel of any one of claims 11 to 19 wherein said steel has 0.2 % yield stress of 75 kg/mm² or more and charpy impact energy of 10 kg-m or more.

25. The method of alore on whelever ball the transmission in from 600 to 100 to 100.

21. A method for manufacturing a high strength martensitic stainless steel comprising the steps of:

5 763 Freparing a martensitic stainless steel consisting essentially of 0.06 wt.% or less © 12 to 16 wt.% Cr, 1 wt.% or less Si, 2 wt.% or less Mn; 0.5 to 8 wt.% Ni) 0.1 to 2.5 wt.% Mo; 0.3 to 4 wt.% Cu, 0.05 wt.% or less N, and the balance being Fe and inevitable impurities;

austenitizing said martensitic stainless steel at a temperature of Ac₃ transformation point to 980 °C to produce a austenitized martensitic steel;

tempering the cooled stainless steel to disperse fine Cu precipitate grains in a matrix at a tempering temperature (T°C) of between 500°C to the lower one of either 630°C or Ac₁ transformation point and at a stempering time ('t' hour'), said tempering temperature and 'said-tempering time satisfying the following equation;

า โท วิ15200 ≦ (201+ logit)(273/1+5T)'เ≦/17800. ชา เช่นสาราช ซีที่ เป็นสังเลย โดยเช่น กับ เสดา เสด โดยเดียก ลหาก ส่ว

- 22. The method of claim 21, wherein said Ac₃ transformation point is from 700 to 850 °C.
- ਸ ਰੋਹੋ.0 mont si legis scalaists soi to thetach ਨੂੰ ਪਾਰ ਸੰਭਾਵਕਾਂ ਵਿੱਚ ਹੈ ਹੈ ਤੇ ਬਾਲੀਆਂ ਨੂੰ ਜਨ ਪ੍ਰਸ਼ਤ ਨਿ ਸਿਰਸੰਸ਼ਕ ਕਰ ਪਾਣ 22. The method of claim 21, wherein said Act transformation point is from 600 to 760 ° C. ਅਤੇ ਆ ਰੋਹੇ ਵ
 - The method of any one of claims 21 to 23, wherein said tempering temperature (To C) and said tempering time (t hour) satisfying the following equation;

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- 25 对 98.9 15500 ≦'(203+ log't)(273位+代T) ≦性7000% To protective of the principle of the protection of the company of the compa
 - 25. The method of any one of claims 21 to 24 wherein the C content of the stainless steel is from 0.013 to as in [0.053 wt]% is any one of any one of the stainless steel is from 0.013 to an info [0.053 wt]% is any one of the stainless steel is from 0.013 to as in [0.053 wt]% is an info stainless of the stainless steel is from 0.013 to as in [0.053 wt]% is an info stainless of the stainless of the stainless steel is from 0.013 to as in [0.053 wt]% is an info stainless of the stainless steel is from 0.013 to as in [0.053 wt]% is a stainless of the stainless of th
- - 27. The method of any one of claims 21 to 26 wherein the Si content of the stainless steel is from 0.14 to 0.47 wt.%.
 - 28. The method of any one of claims 21 to 27, wherein the Mn content of the stainless steel is from 0.05 to 1.05 wt.%.
- 29. The method of any one of claims 21 to 28 wherein the Ni content of the stainless steel is from 0.78 to 7.21 wt.%.
 - 30. The method of any one of claims 21 to 29 wherein the Mo content of the stainless steel is from 0.30 to 2.42 wt.%.
- 31. A method for manufacturing a high strength martensitic stainless steel comprising the steps of:

 preparing a martensitic stainless steel consisting essentially of 0.06 wt.% or less C, 12 to 16 wt.%

 Cr, 1 wt.% or less Si, 2 wt.% or less Mn, 0.5 to 8 wt.% Ni, 0.1 to 2.5 wt.% Mo, 0.3 to 4 wt.% Cu, 0.05 wt.% or less N, at least one element selected from the group consisting of 0.01 to 0.1 wt.% V and 0.01 to 0.1 wt.% Nb and the balance being Fe and inevitable impurities;

austenitizing said martensitic stainless steel at a temperature of Ac₃ transformation point to 980 ° C ¹² to produce a austenitized martensitic steel;

cooling the austenitized martensitic stainless steel;

tempering the cooled stainless steel to disperse fine Cu precipitate grains in a matrix at a tempering temperature (T * C) of between 500 * C to the lower one of either 630 * C or Ac₁ transformation point and at a tempering time (t hour), said tempering temperature and said tempering time 33 satisfying the following equation;

 $15200 \le (20 + \log t)(273 + T) \le 17800.$

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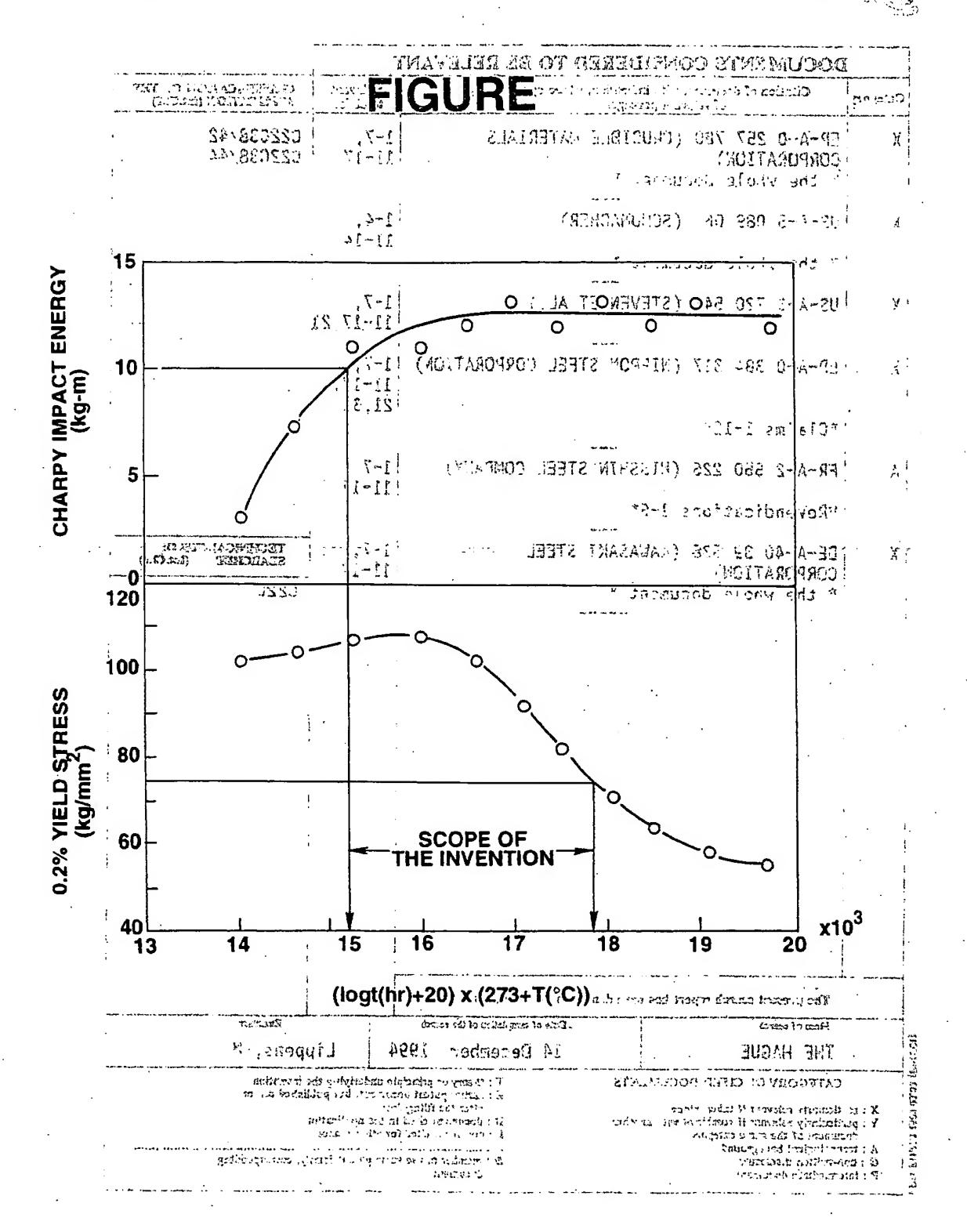
	32.	e method of claim-31/swherein said Acartransformation point is from 700 to 850 °C.	
		The high entire is an entire the impact one of the commence of	
	33.	e method of claim 31, wherein said Ac ₁ transformation point is from 600 to 760 °C.	
_	2 21 . *	io வஞ்சுகள் ஓர்ளவுகை 1 விளையின் கடிய பட்ட உடியிறாளில் முது கரும்பிரமாகள் மிற்கள்களில் படி து method a of Janys one)(of, iclaims ::31 j.to ,33 wherein a said at empering , temperature a (T.A.C) and sai	ч
5		npering time:(-t-hour-):satisfying the:following equation;///2391-0-340/W-S-18-2041-10-34-17	u .
	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	with the content of the balance beauty Forest with impurities,	
	. * 030	500.≦-(20:thriog t)(273] th. T) ≦ 17000. not a manifest stainless officentiate point grainless is	
		ic produce a austeninzed martenaitic steel	
10		e method of any one of claims 31 to 34, wherein the Cicontentrof the stainless steel is from 0.013 to	. O
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		sit in Alino (i) the fireflie for each reviol in the control of the state of the st	· _
	-	e method of any one of claims 31 to 35, wherein the Cr content of the stainless steel iscfrom 12.2 t 8 wt.%.	U
15		O WELLOU.	31
. •		e method of any one of claims 31 to 36 wherein the Sitcontent of the stainless steel is from 0.14 t	.
	(7 wt.%.	
		21038 of 90% ment stated engagement to a table these considered in misco to borneam off. SS	
		e method of any one of claims 31 to 37 wherein the Mn content of the stainless steel is from 0.05 to	
20	•	5. wt.%. If the meriod of claim 21 wherein self Actions of here is from 300 to 760 ft	7.3
	39	e method of any, one of claims 31 to 38 wherein; the Ni content of the stainless steel is from 0.78 t	·
		1 wt.%.	
25		e method of any one of claims 31 to 39 wherein the Mo content of the stainless steel is from 0.30 to 2 wt.%.	(; O;
		- ver Hert al reas avalmatic actific immedia 2 a la real de 15 februara plantes analises antiques de transfer at 17 as	
		e use of high strength martensitic stainless steel according to any one of claims:v1 to:20 in a	ก
	•	vironment containing CO ₂ and/or H ₂ S.	
30		26. The inothed of each one or charas 21 is all with the content of the stanless steel is fig	38
	42.	e use according to claim 41 in drilling or transporting crude oil or natural gas.	
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EUROPEAN SEARCH REPORT

Application Number EP 94 11 6644

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	The present search report has be	en drawn up for all claims X (OS+(i Nicoli	·	
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